

CELLULOSE ESTER FILM AND PRODUCTION METHOD OF THE SAME

FIELD OF THE INVENTION

The present invention relates to a cellulose ester film, and in more detail, to a protective film for a polarizing plate or an optical compensating film, in which optical properties as well as tear strength of the cellulose ester film itself, which is employed in a polarizing plate of a liquid crystal display, is enhanced.

BACKGROUND OF THE INVENTION

Cellulose triacetate film is transparent, has excellent physical and mechanical qualities, and exhibits minimal dimensional variation due to variation of temperature as well as humidity. Heretofore, it has been widely employed as a base for photographic film, drawing tracing film, electrical insulating materials and the like, and recently, has been

employed as a protective film for a polarizing plate of liquid crystal displays or a support for optical compensating films. The cellulose triacetate film employed for the protective film for the polarizing plate of a liquid crystal display element is required to exhibit high light transmission, non-optical orientation, excellent adhesion to polarizing film, excellent flatness, high absorption of ultraviolet radiation, and the like. Further, when employed as the liquid crystal display installed in cars, demanded is excellent durability such as no degradation at high humidity as well as high temperature, excellent dimensional stability, and the like.

The aforementioned cellulose triacetate film exhibits excellent quality such as light transmission, non-optical orientation, and the like. However, since it does not absorb ultraviolet radiation, in order to minimize the degradation of the liquid crystal display due to ultraviolet radiation, UV absorbers are commonly incorporated into the cellulose triacetate film employed as a protective film for the polarizing plate, which is provided on the outermost surface of the liquid crystal display.

In more detail, in the cellulose ester film employed as the protective film for the liquid crystal, fine particles are incorporated to improve ultraviolet radiation resistance

as well as conveyance properties. For instance, Japanese Patent Publication Open to Public Inspection No. 6-130226 describes a technique regarding incorporation of metal oxide particles having a diameter of not more than 0.2 μm ; Japanese Patent Publication Open to Public Inspection No. 10-44327 describes a technique in which particles are applied onto cellulose ester film; and Japanese Patent Publication Open to Public Inspection No. 10-95862 describes a technique in which particles are incorporated and the transparency of the resulting cellulose ester is not degraded. In all of these, film is produced by casting dissolved cellulose ester.

SUMMARY OF THE INVENTION

Incidentally, in the casting, film shrinkage occurs through drying of solvents. By all means, problems occur in which the surface quality of the film is degraded. Thus a means to improve the surface quality is provided during drying or after drying. For example, Japanese Patent Publication Open to Public Inspection No. 4-152125 describes a technique in which drying is carried out while maintaining the width of the film, and Japanese Patent Publication Open to Public Inspection No. 6-278149 describes a technique in which treatment is carried out employing a heated roll as well as a cooled roll. Of these, the dimension retention

drying technique exhibits marked improvement effects and is important. However, when a film containing particles is simply subjected to dimension retention drying, gaps form among the particles and the film, and other problems occur such as degradation of optical properties which increase haze on the film and decrease transmittance, as well as decrease tear strength of the film.

In view of the foregoing, the present invention has been accomplished. An object of the present invention is to provide a cellulose ester film formed by casting, which minimizes degradation of optical properties as well as exhibits sufficient mechanical strength generated by the enhancement of tear strength, and further to provide a production method of the same.

The invention and its embodiments are described below.

The cellulose ester film of the invention comprises particles having aspect ratio of 2 to 7.

The cellulose ester film wherein average particle diameter of the particles is preferably 0.2 to 10 μm .

The cellulose ester film wherein the particles are preferably secondary particles of primary particles having an average particle diameter of not more than 0.2 μm .

The cellulose ester film wherein the particles are preferably primary particles having an average particle diameter of 0.2 to 10 μm .

The cellulose ester film wherein the cellulose ester film comprises particles having average particle diameter of 0.2 to 10 μm , average particle diameter of the particles having aspect ratio of 2 to 7 is 0.2 to 10 μm , the particles having aspect ratio of 2 to 7 is contained not less than 5 wt % of whole particles having average diameter of 0.2 to 10 μm .

The cellulose ester film wherein a haze of the cellulose ester film is not more than 0.6 percent in terms of thickness of 80 μm .

The cellulose ester film wherein at least one side of a dynamic friction coefficient of the cellulose ester film is 0.3 to 1.5.

The cellulose ester film wherein tear strength of the cellulose ester film in terms of thickness of 80 μm is 18 g or more.

The cellulose ester film wherein the cellulose ester film contains 50 weight % or more of lower fatty acid ester of cellulose.

The cellulose ester film wherein the cellulose ester film is a film for the use of liquid crystal display.

The cellulose ester film wherein the cellulose ester film is a protective film for polarizing plate or a optical compensating film.

The cellulose ester film wherein in-plane retardation R_0 of the protective film for polarizing plate or the optical compensating film is not more than 20 nm.

A polarizing plate comprising a first protective film for polarizing plate, a polarizing element, and a second protective film for polarizing plate, wherein the first protective film or the second protective film comprises cellulose ester film, wherein the cellulose ester film comprises particles having aspect ratio of 2 to 7.

A liquid crystal display comprising a first polarizing plate, a liquid crystal cell, and a second polarizing plate provided at inner portion with respect to the first polarizing plate and the liquid crystal cell, wherein the first polarizing plate has a first polarizing element, a first protective film provided on a surface of the first polarizing element which surface is not faced to the liquid crystal cell, and a second protective film provided on a surface of the first polarizing element which surface is faced to the liquid crystal cell,

the second polarizing plate has a second polarizing element, a third protective film provided on a surface of the

second polarizing element which surface is faced to the liquid crystal cell, and a fourth protective film provided on a surface of the second polarizing element which surface is faced to the liquid crystal cell,

wherein at least one of the first, second, third and fourth protective film comprises cellulose ester film, wherein the cellulose ester film comprises particles having aspect ratio of 2 to 7.

A method of preparation of cellulose ester film comprising the steps of, casting cellulose ester comprising particles on a support, heating the cellulose ester on the support, peeling the cellulose ester film from the support, and holding and drying the peeled cellulose ester film, wherein the cellulose ester film after holding and drying comprises particles having an aspect ratio of 2 to 7.

The method of preparation of cellulose ester film, wherein remaining solvent amount is 10 wt % or more when the cellulose ester film is peeled from the support.

The preferred embodiments above will now be described below.

1. A cellulose ester film characterized in comprising flat particles.

The aspect ratio of said flat particles is to be between 2 and 7.

The average particle diameter of said flat particles is to be between 0.2 and 10 μm .

•Said flat particles are to be incorporated into the entire particles, having an average diameter of 0.2 to 10 μm in an amount of at least 5 percent by weight.

•Said flat particles are to be secondary particles of particles having a primary particle diameter of not more than 0.2 μm .

2. A cellulose ester film produced through a process in which said film maintains its width dimension and is dried, characterized in comprising particles having an average particle diameter of 0.2 to 10 μm , and exhibiting a haze of not more than 0.6 percent in terms of thickness of 80 μm , and a dynamic friction coefficient of 0.3 to 1.5.

Preferred embodiments will be described below.

The tear strength of said cellulose ester film is to be at least 18 g in terms of thickness of 80 μm .

The main component of said cellulose ester film is to be lower fatty acid ester.

Said cellulose ester film is to be comprised of lower fatty acid cellulose ester, and is to be prepared by

dissolving said ester in organic solvents through a process which is cooled at -100 to -10 °C and subsequently heated to 0 to 120 °C, and by applying the resulting cellulose ester containing organic solvent solution onto either an endless belt or a drum support.

Said cellulose ester film is to be a protective film for a polarizing plate.

3. In a method for producing a cellulose ester film through a process in which cellulose ester comprising particles is cast onto a support and cellulose ester obtained by peeling from said support is dimensionally retain-dried, a production method of a cellulose ester film characterized in that the residual solvent amount during peeling from said support is at least 10 percent by weight.

The present invention is accomplished to overcome problems in which during casting of a film, optical properties as well as tear strength of said film are degraded by the formation of gaps between the particles and the film due to dimension retention drying of a film, comprising particles. The present inventors paid close attention to the particle shape and achieved the present invention through discovering the following. When small primary particles, having a diameter of no more than $0.2\text{ }\mu\text{m}$, were employed, it

is possible to deform secondary particles into a flat shape, which were formed during dimension retention drying, by controlling the casting speed during casting, the amount of residual solvent during peeling of the film, and the tension while casting the film. As a result, it is possible to minimize gaps between the particles and the film. Further, alternatively, when particles, having a particle diameter of 0.2 to 10 μm , are incorporated, it was discovered that the formation of gaps between particles and the film was minimized by incorporation of flat particles having a particle diameter of 0.2 to 10 μm . Specifically, it was discovered that when the ratio of the residual solvent was at least 10 percent by weight during peeling the film from the support, good results were obtained. Further, it was also discovered that even when particles having a particle diameter of 0.2 to 10 μm , which were not flat, were incorporated, gaps between particles and the film were minimized at an amount of residual solvent of at least 10 percent by weight while peeling of the film from the support.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The cellulose ester film according to the invention comprises flat particles having aspect ratio of 2 to 7.

Listed as cellulose esters based on the present invention are cellulose triacetate, cellulose diacetate, cellulose acetate butyrate, cellulose acetate propionate, and the like. In the case of cellulose acetate, preferably is one having a particular degree of polymerization of 250 to 400 as well as a bonded acetic acid ratio of 54 to 62.5 percent. Cellulose triacetate having a bonded acetate acid ratio of 58 to 62.5 percent of cellulose triacetate is more preferred due to its higher base strength. Cellulose triacetate synthesized from cotton linter and one synthesized from wood pulp may be employed individually or in combination.

The cellulose acetate film preferably contains 50 weight % or more, further preferably 80 weight % or more of lower fatty acid ester of cellulose.

The larger amount of cellulose acetate synthesized from cotton linter, which exhibits better peeling properties from a belt-shaped support (for example, an endless belt), is preferably employed to obtain higher production efficiency. The content ratio of cellulose triacetate synthesized from cotton linter is preferably at least 60 percent by weight because peeling properties are markedly improved at a content ratio of at least 60 percent by weight. The content ratio is

more preferably at least 85 percent by weight, and is most preferably 100 percent by weight.

Commonly, plasticizers are incorporated into cellulose triacetate film. Plasticizers, which may be employed in the present invention, are not particularly limited. However, preferably employed individually or in combination are phosphoric acid ester based plasticizers such as triphenyl phosphate, tricresyl phosphate, cresyldiphenyl phosphate, octyldiphenyl phosphate, diphenylbiphenyl phosphate, trioctyl phosphate, tributyl phosphate, and the like, phthalic acid ester based plasticizers such as diethyl phthalate, dimethoxyethyl phthalate, dimethyl phthalate, dioctyl phthalate, dibutyl phthalate, di-2-ethylhexyl phthalate, and the like, glycolic acid ester based plasticizers such as triacetin, tributyrin, butylphthalylbutyl glycolate, ethylphthalylethyl glycolate, methylphthalylethyl glycolate, butylphthalylbutyl glycolate, and the like. If desired, plasticizers may be employed in combination of two types or more. In this case, the ratio of phosphoric acid ester based plasticizers is preferably not more than 50 percent because in said ratio, cellulose ester film tends not to be subjected to hydrolysis resulting in excellent durability. A lower ratio of phosphoric acid ester based plasticizers is preferred. Either phthalic acid ester based or glycolic acid

ester based plasticizers are preferably employed by themselves.

In the present invention, in order to maintain a water absorption ratio as well as a moisture ratio in the specified range, the added amount of plasticizers is preferably between 3 and 30 percent by weight with respect of cellulose ester, is more preferably between 10 and 25 percent by weight, and is further more preferably between 15 and 25 percent by weight. When the added amount exceeds 30 percent by weight, mechanical strength as well as dimensional stability tends to be degraded.

UV absorbers are preferably incorporated into the cellulose ester film of the present invention. Preferably employed are UV absorbers which are excellent in absorbing ultraviolet radiation having a wavelength of less than 370 nm to minimize degradation of the liquid crystal and absorb as little as possible visible light of wavelengths of more than 400 nm.

In the present invention, the transmittance at a wavelength of 370 nm is particularly to be not more than 10 percent, is preferably not more than 5 percent, and is more preferably not more than 2 percent.

Listed as compounds which are commonly employed are, for example, oxybenzophenone based compounds, benzotriazole

based compounds, salicylic acid ester based compounds, benzophenone based compounds, cyanoacrylate based compounds, nickel complex salt based compounds, and the like. However, examples are not limited to these.

In the present invention, at least one of these UV absorbers is preferably employed, however more than two different UV absorbers may be incorporated in combination.

UV absorbers, which are preferably employed in the present invention, are benzotriazole based UV absorbers, benzophenone based UV absorbers, and the like. Embodiments, in which benzotriazole based UV absorbers with minimal coloration are incorporated into said cellulose triacetate film, are particularly preferred.

In addition thereto triazine based UV absorbers and polymer UV absorbers are employed preferably. Among these the UV absorbers having distribution coefficient of 10.1 or more is employed preferably.

Methods for adding UV absorbers are those in which UV absorbers are dissolved in organic solvents such as alcohol, methylene chloride, dioxolan, and the like, and then added to an organic solvent solution (hereinafter simply referred to as dope) of cellulose ester, or UV absorbers may be directly added to said dope. Inorganic powders, which are insoluble in organic said solvents are dispersed into organic solvents

and cellulose ester employing a dissolver or a sand mill, and are then added to said dope.

The employed amount of UV absorbers in the present invention is commonly between 0.1 and 2.5 percent by weight with respect to the weight of cellulose ester, is preferably between 0.5 and 2.0 weight percent by weight, and is more preferably between 0.8 and 2.0 percent by weight. An amount of UV absorbers, exceeding 2.5 percent by weight, is not preferred due to the tendency of a decrease in transparency.

Employed as solvents for cellulose ester according to the present invention may be, for example, lower alcohols such as methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, cyclohexanedioxanes, lower fatty acid hydrocarbon chlorides, and the like.

A preferred solvent ratio is, for example, 70 to 95 percent by weight of methylene chloride and 5 to 30 percent by weight of other solvents. Further, the concentration of cellulose ester is preferably between 10 and 50 percent by weight.

Production methods of cellulose ester film in the present invention are not particularly limited, and any of the several methods known in the art may be employed. For example, methods, which are described in the following, may be referred to: U.S. Pat. Nos. 2,492,978, 2,739,070,

2,739,069, 2,492,977, 2,336,310, 2,367,603, and 2,607,70; British Patent Nos. 64,071 and 735,892; Japanese Patent Publication Nos. 45-9074, 49-4554, 49-5614, 60-27562, 61-39890, and 62-4208; and others.

Necessary additives such as plasticizers, UV absorbers, and the like, other than cellulose ester and solvents, may be mixed in advance with a solvent and dissolved or dispersed and then placed into a solvent in which cellulose ester is not yet dissolved, or placed into a dope in which cellulose ester has been dissolved.

The heating temperature, after adding the solvent, is preferably higher than the boiling point at one atmosphere of the employed solvent and the temperature at which said solvent does not boil. For example, the temperature is suitably set at least 60 °C and in the range of 80 to 110 °C. Pressure is determined so that the solvent does not boil at the set temperature.

After dissolving cellulose ester, said ester may be removed from the vessel while cooling, or may be removed from the vessel employing a pump and cooled employing a heat exchanger and the like. The removed dope is then supplied for casting. At the time, cooling may be carried out to room temperature. However, cooling is preferably carried out to a temperature which is 5 to 10 °C lower than the boiling point

of the employed solvent, and the cooled dope is employed for casting without varying the resulting temperature because it is possible to decrease the viscosity of the dope.

In the present invention, the best means to obtain cellulose ester film is as follows: a dope which is obtained by dissolving cellulose ester is cast onto a support (a casting process); is heated to remove some of the solvent (a drying process on the support); is peeled from the support; said peeled film is lead to a dimension retention drying process (a film dimension retention drying process); and heat-dried (a film drying process).

The support employed in the aforementioned casting process is comprised of stainless steel in either a belt shape or a drum shape, which is subjected to specular surface treatment. Casting may be carried out on the support in the common temperature range of 0 °C to less than the boiling point of the employed solvent. However, casting is preferably carried out on the support between 5 and 30 °C, because the peel critical time may be increased by gelling the dope. The casting is more preferably carried out on the support between 5 and 15 °C. The peel critical time as described herein means the time during which a cast dope stays on the support at the limit of a casting speed at which

a transparent film with excellent flatness is continually obtained. The peel critical time is preferably as short as possible for excellent productivity to be obtained.

In the drying process, a dope is cast onto the aforementioned support and temporarily gelled. Thereafter, when time between the casting and the peeling is 100 percent, evaporation of solvents is enhanced by setting the dope temperature between 40 and 70 °C within 30 percent of time from the casting to peeling. As a result, peeling is carried out sooner. In order to further increase peeling strength, the dope temperature is preferably set between 55 and 70 °C within 30 percent. Said temperature is preferably maintained within at least 20 percent, and is more preferably maintained within at least 40 percent. Regarding drying on the support, peeling is preferably carried out in such a manner that the dope contains a residual solvent amount of 10 percent or more, and 60 to 150 percent is more preferable because peeling strength from the support decreases. The amount of residual solvent is more preferably between 80 and 120 percent.

When the dope is peeled, the temperature of said dope is preferably set between 0 and 30 °C because it is possible to increase the strength of the base, as well as to minimize

the breakage of the same, and is more preferably set between 5 and 20 °C.

In the present invention, the ratio of residual solvent in film formed on the support is expressed by the formula described below:

Ratio of residual solvent = (mass of residual volatile portion/mass of film after heating process) × 100%

wherein the mass of the residual volatile portion is a value obtained by subtracting the mass of film after the heating process from the mass of film prior to the heating process, when said film is subjected to a heating process at 115 °C for one hour.

In the film dimension retention drying process, the ratio of residual solvent is preferably at least 10 percent by weight while film dimension retention drying, is more preferably at least 15 percent by weight, and is most preferably at least 20 percent by weight. When primary particles having a diameter of 0.2 to 10 μm are not incorporated, the ratio of residual solvent is not limited. However, at least 5 percent by weight is preferred.

Commonly, in the film dimension retention drying process, methods are acceptable in which film is dried while

being conveyed employing a roll loft method, a pin tenter method, or a clip tenter method.

When film is employed as a member for a liquid crystal display, said film is preferably dried while being conveyed employing the tenter method while maintaining its width in order to enhance the dimensional stability. In order to further exhibit effects for enhancement of dimensional stability, maintaining the width is preferably carried out when the ratio of residual solvent is at least 10 percent by weight immediately after peeling the film from the support.

In the film dimension retention drying process after peeling a film from the support, the film tends to shrink in the width direction due to evaporation of solvents. As the film is dried at higher temperature, shrinkage increases. In order to improve the flatness of the resulting film, it is preferable to dry the film while minimizing said shrinkage. For example, as shown in Japanese Patent Publication Open to Public Inspection No. 62-46625, namely, a tenter method is preferred in which total drying or partial drying is carried out in such a manner that the width of the web is maintained by clipping both edges of said web across the width.

During drying a film while maintaining its width by holding both edges, the width may be maintained simply so that the film does not shrink. However, it is preferable to

stretch the film 1.01 to 1.5 times, more preferably 1.03 to 1.2 times in the lateral direction. The stretching is conducted at residual solvent content of preferably 50 wt % or less, and more preferably 35 wt % or less.

The film drying process is a process in which the film, which has been peeled from the support and dried under dimensional retention, is further dried. In order to obtain a film having excellent dimensional stability, the ratio of residual solvent is preferably adjusted to not more than 3 percent by weight, is more preferably adjusted to not more than one percent by weight, and is further more preferably adjusted to 0.5 percent by weight.

Due to deformation of film during the aforementioned film dimension retention drying process, fine particles employed in the present invention are subjected to change in which the shape of the secondary particles in said particles is varied to be flat. As a result, the increase in haze, as well as degradation of transmittance due to shrinkage and deformation of the film, is minimized.

Dry-heating means in the film drying process are not particularly limited, and dry-heating is commonly carried out employing heated air flow, infrared radiation, heated rolls, microwaves, and the like. Heated air flow is preferably employed due to its simplicity. The drying temperature is

preferably in the range of 40 to 150 °C, which is divided into 3 to 5 stages while the temperature is gradually raised to those stages. In order to improve the dimensional stability, drying is more preferably carried out in the range of 80 to 140 °C.

These processes of casting to dimension retention drying may be carried out in an ambience of either air or inert gases such as nitrogen and the like. Of course, the drying ambience is determined taking into consideration the explosion limit concentration of the solvents employed.

Winders, which are employed for the production of the cellulose ester film of the present invention, may be any of those which are commonly employed. Said film may be wound employing a constant tension method, a constant torque method, a tapering tension method, a programmed tension control method in which inner stress is kept constant, and the like.

The thickness of the cellulose ester film according to the present invention is commonly between 20 and 200 μm . However, the thickness is preferably between 20 and 65 μm depending on the demand for a decrease in thickness as well as weight of the polarizing plate employed for LCD, and is more preferably between 30 and 60 μm . The thickness is

further more preferably between 35 and 50 μm . When the thickness is less than these limits, due to a decrease in stiffness of the film, problems due to the generation of wrinkles and the like during the production process of polarizing plates tend to occur. On the other hand, when the thickness is more than said limits, said film contributes less to the decrease in thickness of LCD.

Flat particles as described in the present invention mean those having an aspect ratio of 2 to 7. Said aspect ratio is preferably between 2.5 and 6.5, and is more preferably between 3 and 6.

The aspect ratio as described in the present invention means the average particle diameter/the thickness diameter of the particle. Further, the average particle diameter as described herein means the diameter of a circle having the same area as the projecting area of a particle when the particle is observed vertically for the film surface, employing an optical microscope or an electron microscope. The thickness diameter as described herein means the diameter of a circle having the same area as the projection area when a particle is observed horizontally for the film surface, employing an optical microscope or an electron microscope.

In the present invention, the average particle diameter of particles having an aspect ratio of 2 to 7 is preferably

between 0.2 to 10 μm , is more preferably between 1.0 and 8.0 μm , and is still more preferably between 2.0 and 5.0 μm . Further, particles having an aspect ratio of 2 to 7 may be comprised of secondary particles having an average secondary particle diameter of 0.2 to 10 μm , which are formed by aggregating primary particles having an average primary particle diameter of no more than 0.2 μm , preferably between 5 and 200 nm, and more preferably between 10 and 150 nm, or they may be primary particles having an average particle diameter of 0.2 to 10 μm , which do not form secondary particles. Further, secondary particles having an average secondary particle diameter of 0.2 to 10 μm , which are formed by aggregating primary particles having an average primary particle diameter of no more than 0.2 μm , are preferably incorporated because it is easy to decrease haze. Prior to incorporation into cellulose ester film, particles having an aspect ratio of 2 to 7 may be incorporated.

The ratio of particles, having an average particle diameter of 0.2 to 10 μm as well as an aspect ratio of 2 to 7, is preferably at least 5 percent by weight with respect to all particles having an average particle diameter of 0.2 to 10 μm comprised in cellulose ester film because the effects

of the present invention are more efficiently exhibited. The ratio is more preferably at least 10 percent by weight.

In the cellulose ester according to the present invention, secondary particles having an average particle diameter of 0.2 to 10.0 μm are not formed and deviated particles exist. In such a state, when flat particles are contained among the total particles having an average particle diameter of 0.2 to 10 μm in an amount of at least 5 percent by weight, effects of the present invention are more markedly exhibited. Said amount is preferably at least 10 percent by weight.

Either inorganic compounds or organic compounds may be employed to prepare primary particles which form secondary particles having an aspect ratio of 2 to 7, preferably having an average particle diameter of 0.2 to 10.0 μm , or primary particles (hereinafter referred simply to as fine particles) an aspect ratio of 2 to 7, preferably having a diameter of 0.2 to 10 μm . Listed as examples of inorganic compounds are fine particles of silicon dioxide, titanium dioxide, aluminum oxide, zirconium oxide, and the like. Of these, compounds comprising silicon atoms are preferred, and specifically, fine silicon dioxide particles are preferred. Listed as said fine silicon dioxide particles are, for example, Aerosil 200,

200V, 300, R972, R974, R202, R812, R805, OX50, TT600, R972V and the like, manufactured by Aerosil Co., Ltd.

Listed as organic compounds are acrylic resins, silicone resins, fluoride resins, urethane resins, and the like.

Electroconductive fine particles employed for the antistatic agent may be contained as the particles having an aspect ratio of 2 to 7. According to this, it is preferable since good antistatic property can be obtained with small amount of the antistatic agent, without deteriorating film strength or optical characteristics such as haze increase. Further foreign atom may be incorporated in these metal oxide. For example, Al or In is incorporated in ZnO, Nb or Ta in TiO_2 , Sb, Nb or halogen in SnO_2 . The content of the atom is preferably 0.01 to 25 mol %, and more preferably 0.1 to 15 mol %. Concrete examples of the metal oxide include ZnO, TiO_2 , SnO_2 , Al_2O_3 , In_2O_3 , SiO_2 , MgO, BaO, MoO_2 , Vo. Particularly ZnO, TiO_2 and SnO_2 are preferable.

The electroconductive fine particles having an aspect ratio of 2 to 7 is preferably have volumetric resistivity of not more than 10^7 ohms, particularly not more than 10^5 ohms. Concrete example includes anionic polymer compound, ionen type polymer having dissociate group in main chain, cationic

pendant type polymer having cationic dissociate group in side chain, metal oxide and quaternary ammonium cationic electroconductive polymer having intramolecular crosslink.

In the present invention, the added amount of the aforementioned fine particles with respect to cellulose ester is preferably between 0.04 and 0.3 percent by weight, is more preferably between 0.05 and 0.2 percent by weight, and is most preferably between 0.05 and 0.15 percent by weight.

In the present invention, when a cellulose ester film is cast, a method is listed in which a composition prepared by mixing fine particles with a solvent is processed employing a high pressure homogenizer. Said high pressure homogenizer employed in the present invention is a device which passes a composition, prepared by mixing fine particles with a solvent, in a capillary at high speed to generate special conditions such as high shearing, high pressure state, and the like. When processed employing said high pressure homogenizer, the maximum pressure in the capillary tubes, having a diameter of 1 to 2,000 μm , is preferably at least 100 kgf/cm^2 , and is more preferably at least 200 kgf/cm^2 . Further, at the time, a homogenizer is preferred in which the maximum speed exceeds at least 100 m/second and the maximum rate of heat transfer exceeds at least 100 kcal/hour.

Listed as high pressure homogenizers, as described above, are an ultra-high pressure homogenizer (under the trade name of Microfluidizer) manufactured by Microfluidics Corporation, and Nanomizer manufactured by Nanomizer Co. In addition to these, listed are a Manton-Gaulin type high pressure homogenizer, for example, Homogenizer manufactured by Izumi Food Machinery, and the like.

In the present invention, a cellulose ester film is advantageously obtained employing the method described below. Fine particles are dispersed into a solvent comprising lower alcohols in an amount of 25 to 100 percent by weight, and the resulting mixture is mixed with a dope prepared by dissolving cellulose ester in a solvent; the resulting mixture is then cast onto a support, and subsequently dried. The content ratio of lower alcohol is preferably between 50 and 100 percent by weight, and is more preferably between 75 and 100 percent by weight. Preferably listed as lower alcohols are methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, and the like. Solvents other than lower alcohols are not particularly limited. However, solvents are preferably employed which are used during casting cellulose ester.

In the present invention, fine particles are preferably dispersed into a solvent at a concentration of 1 to 30

percent by weight. Dispersion exceeding the upper limit of the concentration is not preferred due to rapid increase in viscosity. The concentration of fine particles in a dispersion is preferably between 5 and 25 percent by weight, and is more preferably between 10 and 20 percent by weight.

Further, the haze of the cellulose ester film of the present invention is preferably no more than 0.6 percent in terms of a thickness of 80 μm . Further, the dynamic friction coefficient of at least one surface of the cellulose ester film is preferably between 0.3 and 1.5. The dynamic friction coefficient of both surfaces of the polyester film is more preferably between 0.3 and 1.5. Still further, the tear strength is preferably at least 18 g, in terms of a thickness of 80 μm .

Further, in case the cellulose ester film of the present invention is employed as a film for liquid crystal displays such as the protective film for a polarizing plate, optical compensation film (including a visual field enlarging film, phase difference film, color compensation film, contrast improving film, luminance improving film and the like), and the like, said cellulose ester film preferably has an inner surface retardation R_0 of less than 20 nm.

In the present invention, the haze, in terms of the film thickness of 80 μm , may be measured employing an ASTM-

D1003-52. Said haze is commonly between 0.0 and 0.6 percent, is preferably between 0.0 and 0.4 percent, and is more preferably between 0.1 and 0.2 percent.

In the present invention, the dynamic friction coefficient of both surfaces of a film may be measured employing a method specified in JIS-K-7125 (1987). In this case, however, when metal such as a rigid ball is employed as a friction measuring material during measurement of the dynamic friction coefficient of a film, it is impossible to confirm the effects of the addition of fine particles in the film. Accordingly, it is necessary that the dynamic friction coefficient between films is measured without fail. Thus, according to the aforementioned JIK-K-7125, measurement may be carried out in such a manner that films are used as a sample as well as a friction measuring material and arrangement is carried out so that the front surface and the reverse surface of films come into contact. In the present invention, the dynamic friction coefficient of both film surfaces is between 0.3 and 2.5, is preferably between 0.5 and 1.3, and is more preferably between 0.6 and 1.0.

Inner surface retardation R0 can be obtained by employing an automatic double refractometer, for example, Kobra-21ADH (manufactured by Oji Keisokukiki Co., Ltd.), in such a manner that at a wavelength of 590 nm, the three-

dimensional double refractive indices are measured, and the obtained refractive indices N_x , N_y , and N_z are used for calculating the double refractive index, wherein N_x is the refractive index in the delayed phase axis direction within the film surface, N_y is the refractive index in the advanced phase axis direction within the film surface, and N_z is the refractive index in the layer thickness direction, while "d" represents the film thickness (in nm).

$$R_0 = (N_x - N_y) \times d$$

$$R_t = \{(N_x + N_y)/2 - N_z\} \times d$$

Inner surface retardation R_0 is preferably less than 20 nm, is more preferably less than 5 nm, and is most preferably between 0 and 1 nm.

Further, a film having a retardation value R_t in the film thickness direction of 30 to 300 nm is preferably employed and specifically a film having 50 to 150 nm is preferably employed.

In the cellulose ester film of the present invention, those, which satisfy the relationship described below, are most preferably employed:

$$P \leq 1 - \sin^2(2\theta) \cdot \sin(\pi R_0/\lambda)$$

wherein P is 0.999, θ is the angle of the delayed phase axis direction within the surface with respect to the longitudinal

direction of the film, R_0 is the retardation, and λ is the light wavelength of 590 nm during 3-dimensional refractive index measurement to obtain R_0 and θ .

In the present invention, the cellulose ester film is preferably subjected to a so-called knurling treatment in such a manner that unevenness is provided to both edges of said film across the width so as to increase the apparent thickness of the edges.

$$X \text{ (in percent)} = (a/d) \times 100$$

wherein a (in μm) is the height of knurling, d (in μm) is the film thickness, and X (in percent) is the ratio. X is set in the range of 0 to 25 percent, is preferably between 0 and 15 percent, and is more preferably between 0 and 10 percent. Exceeding the upper limit of the knurling height ratio is not preferred because vortex-shaped deformation tends to occur, while a smaller ratio is also not preferred because winding properties are degraded.

Herein, cellulose ester film is most suitably produced in such a manner that cellulose ester, comprising particles, is cast onto a support; some of the solvent is removed upon heating; thereafter, the resulting cellulose ester film is peeled from said support; is passed through a dimension retention drying process (in which the width is maintained);

and then passed through a drying process. In order to further enhance effects of dimensional stability, the dimension retention drying is preferably carried out at conditions in which the amount of residual solvent is at least 10 percent by weight during peeling of said ester film from the support.

In the present invention, foreign substances in cellulose ester film are preferably minimal. Specifically, foreign substances, which are observed at a polarized light cross Nicol state, are preferably minimal. The foreign substances, which are observed at a polarized light cross Nicol state, mean those which are observed in such a manner that two polarizing plates are arranged at a right angle (cross Nicol) state and said cellulose film is placed between them. Such foreign substances at said polarized light cross Nicol state are observed only as a luminescent spot caused by penetrating light from opposite side under light shielded conditions. Thus it is possible to readily identify the size as well as the number of foreign substances.

The number of foreign substances having a size of 5 to 50 μm per 250 mm^2 , which are observed under a polarized light cross Nicol state, is preferably not more than 200, and the number of foreign substances having a size of at least 50 μm is preferably 0. The number of foreign substances having a

size of 5 to 50 μm is more preferably not more than 100, and is further more preferably not more than 50.

In order to obtain cellulose ester film comprising minimal foreign substances as described above, any means may be employed. However, the cellulose ester film comprising minimal foreign substances is obtained by filtering a dope composition prepared by dissolving cellulose ester in a solvent, employing the filter paper described below. In this case, said dope composition is filtered at a filtration pressure of not more than 16 kg/cm^2 , employing any of the several types of filter paper which preferably exhibit a water filtration time of at least 20 seconds, and said dope is subsequently cast. Said dope composition is more preferably filtered at a filtration pressure of not more than 12 kg/cm^2 , employing a filter paper exhibiting a water filtration time of at least 30 seconds. Said dope composition is more preferably filtered at a filtration pressure of not more than 10 kg/cm^2 , employing a filter paper exhibiting a water filtration time of at least 40 seconds. Further, at least two said filter papers are preferably employed as a pair. The filtration pressure may be controlled upon suitably selecting the rate of filtration flow as well as the filtration area.

The preparation method of a polarizing plate obtained employing the cellulose ester film of the present invention is not particularly limited, and it may be prepared employing common methods. For instance, one is a method in which cellulose acetate film, which has been subjected to alkali treatment, is adhered onto both surfaces of a polarizing film prepared by immersing it in an iodine solution and then dimension retention drying, while employing an aqueous solution of completely saponified-type polyvinyl alcohol. In order to enhance adhesion, instead of using said alkali treatment, employed may be methods as described in Japanese Patent Publication Open to Public Inspection Nos. 6-94915 and 6-1182432.

The cellulose ester film according to the invention is suitable for employing as a material of a liquid crystal display apparatus such as film for a liquid crystal display apparatus. A member for liquid crystal display means one which is employed in a liquid crystal display apparatus. For example, listed are a polarizing plate, a protective film for a polarizing plate, a phase difference plate, a reflection plate, a visibility angle enhancing film, a glare minimizing film, a non-reflection film, an antistatic film, and the like. Of these, the present invention is more preferably applied to a polarizing plate, a protective film for a

polarizing plate, a phase difference plate, and a visibility angle enhancing film, which are subjected to severe demands for dimensional stability.

The polarizing plate of the present invention will now be described. The polarizing plate of the present invention is structured in such a manner that a polarizer is placed between the first protective film for the polarizing plate and the second protective film for the polarizing plate.

Either the protective film for the polarizing plate or the second protective film for the polarizing plate (preferably both protective films) comprises cellulose ester film which comprises particles having an aspect ratio of 2 to 7.

Further, the polarizer is preferably obtained in such a manner that iodine or dye is adsorbed onto a film comprised of polyvinyl alcohol and the like, and the resulting film is subsequently stretched.

Next, one example of the liquid crystal display of the present invention will be described with reference to Fig. 1. The liquid crystal display of the present invention comprises first polarizing plate 31, liquid crystal cell 4, and second polarizing plate 32 which is provided toward the interior of both said first polarizing plate 31 and said liquid cell 4. Further, back light 5 may be provided as the light source

toward the interior of second polarizing plate 32. Said first polarizing plate 31 comprises first polarizer 110 and first protective film 21 provided on the surface of said first polarizer 110 on the side which does not face liquid cell 4, and second protective film 22 provided on the surface of said first polarizer 110 on the side which faces liquid cell 4. Further, second polarizing plate 32 comprises second polarizer 120, third protective film 23 provided on the surface of second polarizer 120 on the side which faces liquid cell 4, and fourth protective film 24 provided on the surface of second polarizer 120 on the side which does not face liquid cell 4. Further, at least one of first protective film 21, second protective film 22, third protective film 23, and fourth protective film 24 (preferably all protective films) comprises cellulose ester film, which comprises particles having an aspect ratio of 2 to 7.

EXAMPLES

The present invention is specifically described with reference to examples below. Further, "parts" below is "parts by weight", unless otherwise specified.

Example 1

•Preparation of Sample 1

1. Preparation of Dispersion A

Ethanol 27 parts

Particles 1 (fine silicon dioxide particles) (under the trade name of Aerosil 200V with a primary particle diameter of 15 nm, manufactured by Nihon Aerosil Co., Ltd)

3 parts

were mixed and stirred at 500 rpm for 30 minutes.

Thereafter, the resulting mixture was dispersed at a pressure of 200 kgf/cm² employing a Manton-Gaulin type high pressure homogenizer to prepare Dispersion A.

2. Preparation of Addition Composition A

Aforementioned Dispersion A 22 parts

Cellulose triacetate synthesized from cotton linter 12 parts

2-(2'-hydroxy-3',5'-di-t-butylphenyl)benzotriazole (UV Absorber 1) 26 parts

Methylene chloride 290 parts

The aforementioned Addition Composition A was measured employing a centrifugal type particle distribution meter (CAPA500, manufactured by Horiba Seisakusho Co., Ltd.), whereby 1.2 μ m was found to be the average particle diameter of Particles 1 (fine silicon dioxide particles).

3. Dope Composition A

Cellulose triacetate synthesized
from cotton linter (having
an acetylation degree of 61.0
percent) 85 parts

Cellulose triacetate synthesized
from wood pulp (having an
acetylation degree of 61.0
percent) 15 parts

Ethylphthalylethyl glycolate
(plasticizer) 4 parts

Methylene chloride 475 parts

Ethanol 50 parts

Dope Composition A consisting of the above components was placed in a sealed vessel, heated up to 70 °C, and totally dissolved while stirring to obtain Dope Composition A. Four hours were required for dissolution. After filtering Dope Composition A, said Dope Composition A and Addition Composition A were blended employing an in-line mixer so that the addition ratio of fine particles to cellulose triacetate was 0.05 percent by weight. Thereafter, the resulting dope, maintained between 30 and 35 °C, was uniformly cast onto a stainless steel band support employing a belt casting apparatus. Said dope was dried to within the

range at which said dope was capable of being peeled, and then peeled from the stainless steel band support. At the time, the amount of residual solvent in the dope was 25 percent. Three minutes were required from dope casting to its peeling.

After the dope was peeled from the stainless steel band support, it was conveyed by many rolls while maintaining the width, through dry-heating zones consisting of a first zone at 50 °C, a second zone at 90 °C, and a third zone at 120 °C. Drying was then completed at a dry-heating zone at 130 °C. The resulting film was subjected to knurling treatment at both edges to a width of 10 mm and a height of 4 μm . Thus Cellulose Triacetate Film Sample 1, having a thickness of 40 μm , was prepared.

The film width was determined to be 1,300 mm, and the roll length was determined to be 3,000 m. Regarding winding tension, the initial tension was determined to be 20 kg/1,300 mm, while the final winding tension was determined to be 10 kg/1,300 mm.

•Preparation of Samples 2 through 4

Samples 2 through 4 were prepared in the same manner as Sample 1, except that the amount of the residual solvent was varied by varying time from dope casting to peeling, and

further particle conditions were varied as shown in Table 1. Sample 5 was prepared in the same manner, except that Aerosil 200V was replaced with SYLISIA 350 (having an average particle diameter of 1.8 μm , and manufactured by Fuji SYLISIA CHEMICAL LTD.).

Film Samples 1 through 5, prepared as described above, were subjected to the performance evaluation described below. Table 1 shows the obtained results.

(Evaluation Methods)

•Average Particle Diameter and Aspect Ratio

A particle was observed employing a scan-type electron microscope (capable of a magnification factor of 3,000), and the diameter of a circle circumscribing said particle was determined to be the diameter of said particle. Further, 100 particles in random areas were observed, and the resulting average diameter was designated as the average particle diameter (a primary particle diameter or a secondary particle diameter). Further, the aspect ratio was obtained employing the resulting average diameter.

•Haze

Haze was measured in accordance with ASTM-D1003-52.

•Dynamic Friction Coefficient

The dynamic friction coefficient between the front surface of a film and the reverse surface of another film was

measured in accordance with JIS-K-7125 (1987) in such a manner that films were cut so that the front surface and the reverse surface were brought into contact; loaded at a weight of 200 g; said weight was horizontally dragged along the surface of the sample moving at a velocity of 100 mm/minute and over a contact area of 80 × 200 mm; and an average load (F) during movement of said weight was measured. The dynamic friction coefficient (in μm) was then obtained by the formula described below:

Dynamic friction coefficient = F (in gf)/weight of the weight (in gf)

•Surface Quality

The surface quality was visually evaluated, based on the standard described below:

- A: unevenness is barely observable on the surface and is at a level which does not cause any problem as a commercial product.
- B: slight unevenness is observed on the surface and is also at a level which causes no problem as a commercial product.
- C: unevenness is clearly observed on many areas on the surface and is at a level which is not viable as a commercial product.

Table 1

Sam- ple	Primary Particle Diameter	Secon- dary Particle Diameter	Main- tained Width	Ratio of Residual Solvent before Maintain- ing (in %)	Aspect Ratio	Haze	Dynamic Friction Coeffi- cient	Quality	Remarks
1	15 nm	2.5	applied	25	4.5	0.1	0.8	A	Inv.
2	15 nm	2.4	applied	15	4.0	0.2	0.8	A	Inv.
3	15 nm	2.2	applied	10	3.1	0.3	0.7	A	Inv.
4	15 nm	2.5	applied	5	2.0	0.4	0.8	B	Inv.
5	1.8 μ m	-	applied	-	1.5	0.3	1.8	C	Comp.

Inv.:present invention Comp.:comparative example

As can clearly be seen from Table 1, it is found that Sample 5, comprising no flat particles, exhibits degradation of surface quality to such a degree that the dynamic friction coefficient is higher and further unevenness is clearly observed on the film surface. It is to be noted that Sample 5 was not subjected to dimension retention drying across its width and contained a lower amount of residual solvent in the film, and thus such degradation is due to the fact that particles are not shaped to be flat.

Example 2

Samples 21 through 25 were prepared in the same manner as Example 1, except for the following: in the dope composition in Example 1, methylene chloride was replaced with the same amount of methyl acetate as shown in the composition described below:

Ethylphthalylethyl glycolate

(plasticizer)

4 parts

Methyl acetate

475 parts

Ethanol

50 parts

were to be cooled between -100 and -10 °C. Subsequently, the remaining cellulose triacetate was added and was totally dissolved in an organic solvent during heating from 0 °C to 120 °C. The resulting dope was blended with Addition

Composition A in the same manner as Example 1, employing an in-line mixer. The resulting samples were subjected to the same evaluation as Example 1. Table 2 below shows those obtained results.

Table 2

Sam- ple	Primary Particle Diameter	Secon- dary Particle Diameter	Main- tained Width	Ratio of Residual Solvent before Maintain- ing (in %)	Aspect Ratio	Haze	Dynamic Friction Coeffi- cient	Quality	Remarks
21	15 nm	2.5	applied	25	4.5	0.1	0.8	A	Inv.
22	15 nm	2.4	applied	15	4.0	0.2	0.8	A	Inv.
23	15 nm	2.2	applied	10	3.1	0.2	0.7	A	Inv.
24	15 nm	2.5	applied	5	2.0	0.3	0.8	B	Inv.
25	1.8 μ m	-	applied	-	1.5	0.2	1.8	C	Comp.

Inv.:present invention Comp.:comparative example

As can clearly be seen from Table 2, regarding samples prepared by varying the production method for the dope composition, it is found that Sample 25, comprising no flat particles, exhibits the degradation of surface quality to such a degree that the dynamic friction coefficient is higher, and further, unevenness is clearly observed on the film surface.

In Examples according to the invention tear strength in terms of thickness of 80 μm was 18 g or more. In-plane retardation R0 of the samples according to the invention was not more than 20 nm.

According to the present invention, markedly excellent effects are exhibited in which the degradation of optical properties of cellulose ester film formed by casting can be minimized, and at the same time, sufficient mechanical strength due to enhancement of tear strength of said film can be provided.

Disclosed embodiment can be varied by a skilled person without departing from the spirit and scope of the invention.